

SHOCK TUBE STUDIES OF IGNITION CHARACTERISTICS OF SOME LIQUID HYDROCARBONS

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The high temperatures and high exothermicity of combustion reactions in general have made the experimental study of these reactions especially difficult. When problems arise in the manifold practical applications of combustion, the lack of fundamental information on the processes which are involved leave only empirical methods with which to arrive at a solution. Some of the unique characteristics of the shock tube make it especially useful in overcoming the experimental difficulties in combustion studies. A number of investigations have already been made in which advantage has been taken of this device.

For the spark-ignition engine, knock, surface ignition, and rumble are some specific problems which would profit from appropriate fundamental studies. Two characteristics of the shock tube which make it useful for these applications are the freedom from surface effects and the instantaneous heating to a selected high temperature which is possible. Because of these advantages, a shock tube study of the ignition of hydrocarbon-oxygen mixtures was begun.

The earlier work in this area by Gay and others is listed by Steinberg and Kaskan¹; this paper, and the discussion thereto, very well delineates the pitfalls and necessary precautions for the study of ignitions in the shock tube. The more satisfactory results with ignition by the reflected shock wave and the importance of surface discontinuities in causing anomalous behavior are described. Ignition in a reflected shock wave has been used to investigate ignition of a spray of Diesel fuel². A study of the high-temperature ignition characteristics of different fuels was made by Mullins³ in a system in which was designed to approximate combustion conditions in a jet engine. The differences between a number of liquid fuels in reaction with oxygen in a shock tube at intermediate temperatures has been studied by Malmberg and Wellman. In the present investigation, various characteristics of the ignition of several liquid hydrocarbons with oxygen were studied in the reflected shock wave.

EXPERIMENTAL

Some earlier experiments had shown that the response of a piezoelectric pressure pickup is noticeably different to an explosion as compared to an initial and reflected shock wave. The apparatus was constructed to utilize the reflected shock wave, with, in general, the detecting elements located in the endplate of the reaction section.

The shock tube was made from one-inch Schedule 40 stainless steel pipe, with necessary connections for evacuation, filling, and instrumentation. Helium was used as a driver gas. Mylar film, ranging in thickness from 0.0035 to 0.030 inch was used for the diaphragms. The tube was designed with a factor of safety of ten; the peak pressures observed in explosions corresponded with the peak pressure calculated by assuming instantaneous liberation of the energy. For most of these experiments, a four-foot driver section and a three-foot reaction section was used. With the pressures used in these experiments, the time available for reaction at the far end of

the reaction section (before arrival of the rarefaction or a re-reflection from the contact front) was always greater than the longest ignition delays measured.

A miniature SLM quartz piezoelectric pressure pickup and a quartz window were mounted in the endplate; the window, which led to a 1P28 photomultiplier tube looked down the shock tube toward the high pressure section. With the photomultiplier housing rigidly attached to the shock tube, anomalous deflections can be obtained at the time of breaking of the diaphragm and somewhat less pronounced at the time of reflection. Shock-proof mounting of the tube solved this problem. The first deflection is presumably shock transmitted through the metal of the tube. This behavior may be the explanation of the "light" observed by Steinberg and Kaskan in initial shock waves in which there was no ignition.

The output from the pressure pickup was sent into a Kistler Piezo calibrator and thence to one input of a Tektronix 531 oscilloscope with a Type CA dual-trace plug-in unit. A single sweep of the oscilloscope was triggered from the breaking of the diaphragm.

The explosive mixtures were made by the method used by Steinberg and Kaskan¹⁾, flow of oxygen and the fuel vapor each through a critical velocity orifice flow-meter. The method was modified so that mixtures could be made from liquid hydrocarbons. The orifices, a reservoir for hydrocarbon vapor, and a pressure gauge on the reservoir were held in a constant-temperature oven at 125°. After the gases were mixed, the hydrocarbon was below its vapor pressure at room temperature so that it could be led into the evacuated shock tube.

The temperatures which are used in the discussion of results are read from a curve made for each hydrocarbon; the temperature was calculated from the diaphragm pressure ratio by the usual shock wave relations. The specific heat ratio for the components was assumed constant, and the values of temperature may be as much as 20 percent high. The necessary data, in general, are not available for more accurate calculations for these hydrocarbons. However, for our purposes, the relative values are the point of interest, and there should be no important deviation in that respect.

The measurement of length of time before ignition, the "ignition delay", was made on the two simultaneous traces. An example is shown in Figure 1A. The lower trace is of the pressure transducer; the small initial rise is the arrival-reflection of the shock. The second sharp high rise is the explosion, sometimes called a "retonation wave". The upper trace, recorded by the photomultiplier, confirms the occurrence of the explosion. Variations in this trace will be discussed later.

RESULTS

The measurement of delay time was characterized by a relatively large scatter of points, similar to earlier results¹⁾. Two examples are shown, Figures 2 and 3, isooctane and benzene respectively. The large number of points are available for benzene because a number of auxiliary studies were made with that hydrocarbon. The photomultiplier trace shown in Figure 1A is for a high temperature; i.e., a short delay. The small or non-existent "overshoot" of initial emission of light is characteristic of the high temperature. As the temperature is lowered, the amount of overshoot is much greater preceding the leveling off which seems to characterize the explosion (Figure 1B). Hence, for benzene, a number of points are shown in which flame was observed almost exclusively (Figure 1C), plus a number with a large amount of flame, plus some explosion. The consistent behavior in a large number of experiments, including the useful data from the pressure transducer, the results of experiments with a second pressure transducer in the side wall six inches from the end, and experiments with a quite slow writing speed, all confirm these interpretations. The high luminosity of the flame compared to the explosion is quite striking

when the relative rates of the reactions are compared. Rough measurements indicate that the time required for the explosion to reach the pressure transducer six inches from the end is roughly one-tenth the time required for the reflected shock to arrive.

Whether explosion or flame was observed, the lowest temperature at which reaction would occur was quite characteristic of a given hydrocarbon. The results for a limited number of fuels are given in Table I. The behavior of these fuels in high-temperature ignition is remarkably parallel to the tendency to produce rumble; hence, the LIB number for each fuel is given in the table as well (Isooctane, high resistance to rumble, LIB number equals 100; benzene, zero).

TABLE I
MINIMUM TEMPERATURE OF IGNITION FOR STOICHIOMETRIC
MIXTURES OF VARIOUS FUELS WITH OXYGEN

<u>Fuel</u>	<u>Minimum Temperature* of Ignition, °K</u>	<u>LIB Number **</u>
Pentane	1350	***
Isooctane	1340	100
Toluene	1220	50
Benzene	1155	0
Benzene-isooctane 1:1	1250	50
Toluene-isooctane	1250	
Benzene-water 1:1	1350	

* Conditions under which ignition occurred in about half the attempts.

** LIB numbers are determined with lead necessarily present. The benzene isooctane 1:1 mixture is LIB = 50 by definition of the scale.

*** Not measurable because of its octane number; probably about 100.

A number of experiments were performed to determine the effect of volatile additives on the minimum temperature of ignition of benzene-oxygen mixtures. The number of experiments in each case is not large enough for an accurate determination of the 50 percent point, but the following preliminary observations were made. Conventional motor mix with tetraethyl lead has a relatively small effect on the minimum temperature of ignition. The temperature was raised appreciably with tertiarybutyl acetate present in 0.5 percent amount. Tetramethyl lead in a motor mix quite definitely increased the minimum temperature of ignition.

DISCUSSION

The ignition delay and the minimum temperature of ignition are measures of reactions between hydrocarbons and oxygen which lead to a condition that engenders rapid combustion by flame or explosion. The values of the ignition delay are not particularly useful experimental results because of the large amount of scatter, although there is appreciably less scatter for the aromatics. Part of the data from benzene-oxygen experiments was used for calculation of rate constants. From data such as shown in Figure 2, the rate constants will necessarily have a range of values. However, good agreement was obtained among the rate constants which were calculated when the rate expression included only fuel concentration to the first power as compared to the values when the product of the fuel and oxygen concentrations each to the first power was used. This result is not surprising when it is considered that the reaction under study is an initiation and the mixture is stoichiometric; i.e., 7.5 moles of oxygen per mole of hydrocarbon. The data in Figures 2, 3 and 4, are presented as Arrhenius plots for convenience and for comparison to results of others. An activation energy calculated from the slope of

the best "line" is based on the assumption that this initiation reaction leads to a critical concentration of some active species, and this concentration is the same at all temperatures. Values from 10 to 40 kcal/mole are obtained; clearly, the assumption is not generally valid in these cases. The values of the temperatures are in error to a certain extent, as already discussed. However, in some earlier work⁴⁾ in which the temperature was obtained by a more accurate method, the beginning of the reversal of the relative ease of oxidation of aromatic, as compared to paraffin hydrocarbons, was observed at 900-950°K. The approximate calculated temperatures in the present work fit this general pattern within the possible error. In addition, these results in the "crossing over" region are in agreement with the findings of the present investigation.

The minimum temperature of ignition is shown on Figures 2, 3, and 4, because it demonstrates more concretely the reality and validity of this number. There are a few isolated cases of explosion below the limit; however, these were found in a large number of experiments in which no reaction occurred. In addition, when ignition did occur below this borderline area, it usually was marked by some quite different characteristics.

As the representative traces in Figure 1 indicate, the explosion in general seems to develop from a flame, except at high temperatures the preliminary spike is almost lost. These combustion reactions are necessarily homogeneous. The known facts of surface ignition and LIB requirements may be examined from this viewpoint. The correlation of the minimum temperature of ignition with the LIB number suggests that the characteristic tendency of aromatic fuels to produce rumble may result from a greater ease of the undesired premature ignition from an area of deposit which is active in surface ignition. This ignition need result only from a local heating. If this interpretation is valid, the complexity of the problem of surface ignition may be considerably reduced in that the fuel need not necessarily enter directly into the reactions in the deposit. Rather, the interaction of the deposit and oxygen is paramount. This view is consistent with results from the measurements of temperature of ignition of engine deposits in an atmosphere of oxygen; a low temperature of ignition is correlated with a high LIB requirement for the engine in the test in which the deposit was formed.⁵⁾ A fuel is not present in these experiments.

The experiments with one mole of water present with benzene in the stoichiometric mixture with oxygen confirms the importance of the homogeneous reaction in rumble. In an engine, the addition of this amount of water to the benzene fuel eliminates the rumble. In the shock ignition experiments, correspondingly, the presence of water increased the minimum temperature of ignition for benzene to the value for isooctane. Even at very high temperatures, the presence of water caused many of the ignitions to be largely flame rather than explosion.

The experiments with additives were not as definitive as would be desired, largely because a reliable determination requires a relatively high number of individual determinations. Also, a diaphragm-breaking apparatus, now being built, will allow more flexibility in the control of the diaphragm-breaking pressure. This method in general offers considerable promise as a means of studying in more detail the conditions leading to explosion. If, for example, in the borderline region differences can be detected spectroscopically or by some other method between mixtures that explode rather than burn with a flame, very useful information would be forthcoming.

In general, other aspects of the investigation are similar to results already described. Almost all of the experiments were run with 100 mm pressure in the reaction section. Small changes in reaction pressure and small changes from stoichiometric composition had only small effects. The exposed surface of the miniature pressure pickup had rather sharp corrugations. The surface discontinuities at this point and small irregularities around the window were very satisfactorily eliminated by smoothing on Apiezon Sealing Compound Q. A number of experiments were performed with pentane and air rather than oxygen. The delay times were, in general,

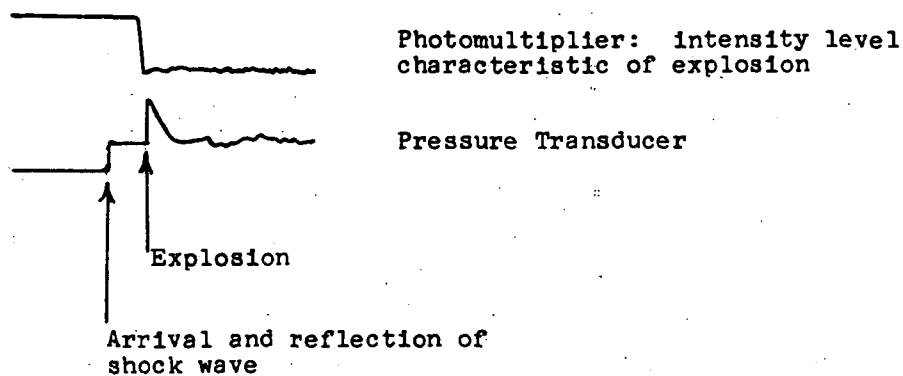
a bit longer, as might be expected, but otherwise these limited experiments showed no important differences.

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A. High temperature: short delay time, explosion



B. Intermediate temperature: flame appears initially



C. Low temperature: mostly flame, weak explosion

Fig. 1. Representative oscilloscope traces from which delay time and other experimental variables were determined. Writing speed, 200 μ sec./cm; trace 10 cm in length. Vertical amplification unchanged in these experiments.

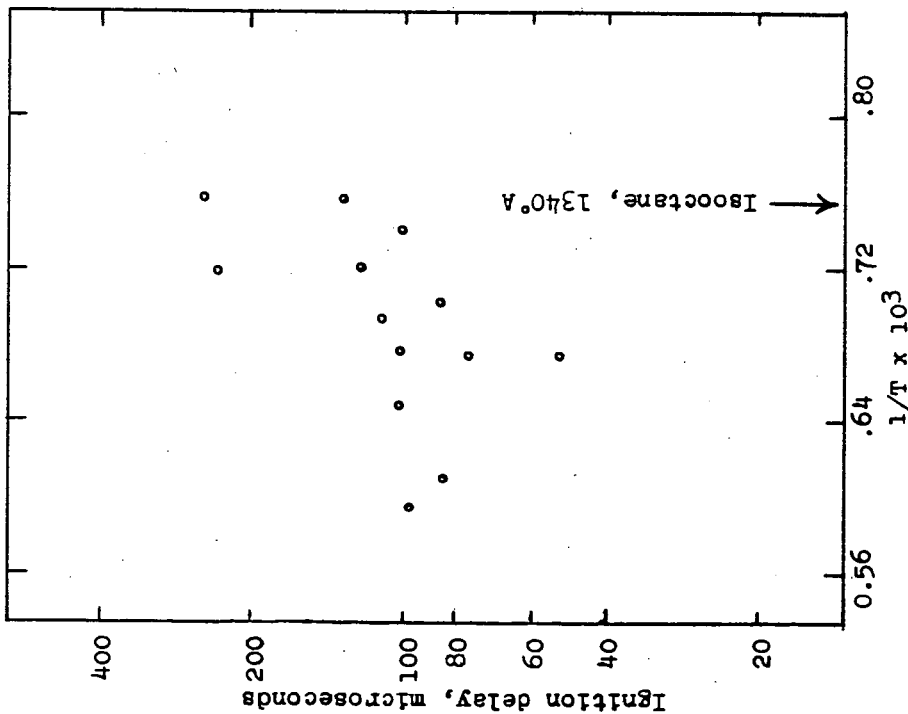


Fig. 2. Characteristic results in the ignition of isooctane-oxygen; logarithm of the ignition delay versus reciprocal of the absolute temperature.

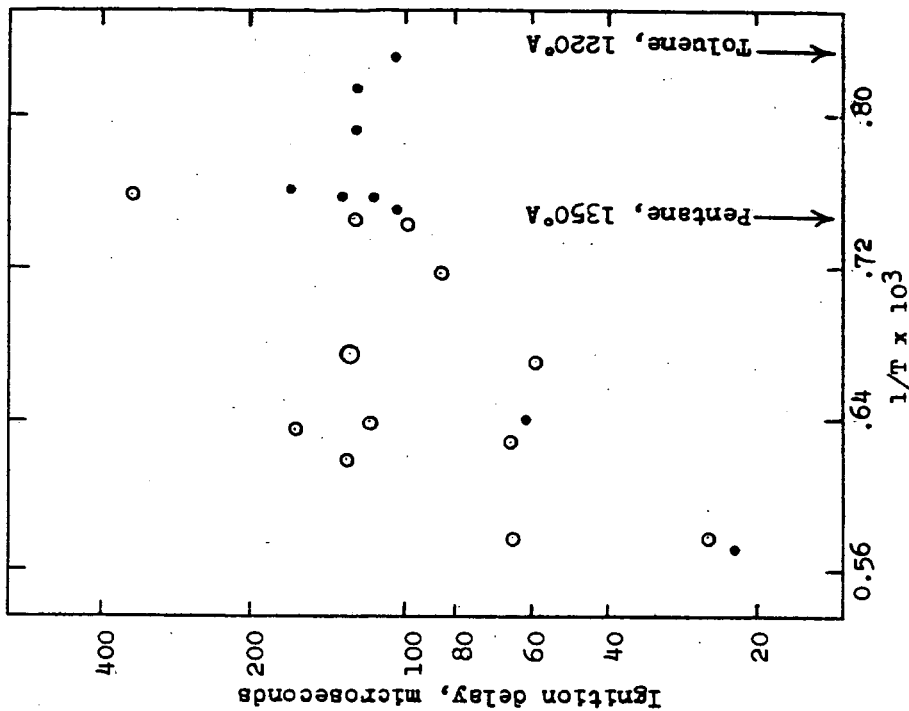


Fig. 4. Ignition of pentane-oxygen and toluene-oxygen; logarithm of the ignition delay versus the reciprocal of the absolute temperature. O Pentane; • Toluene

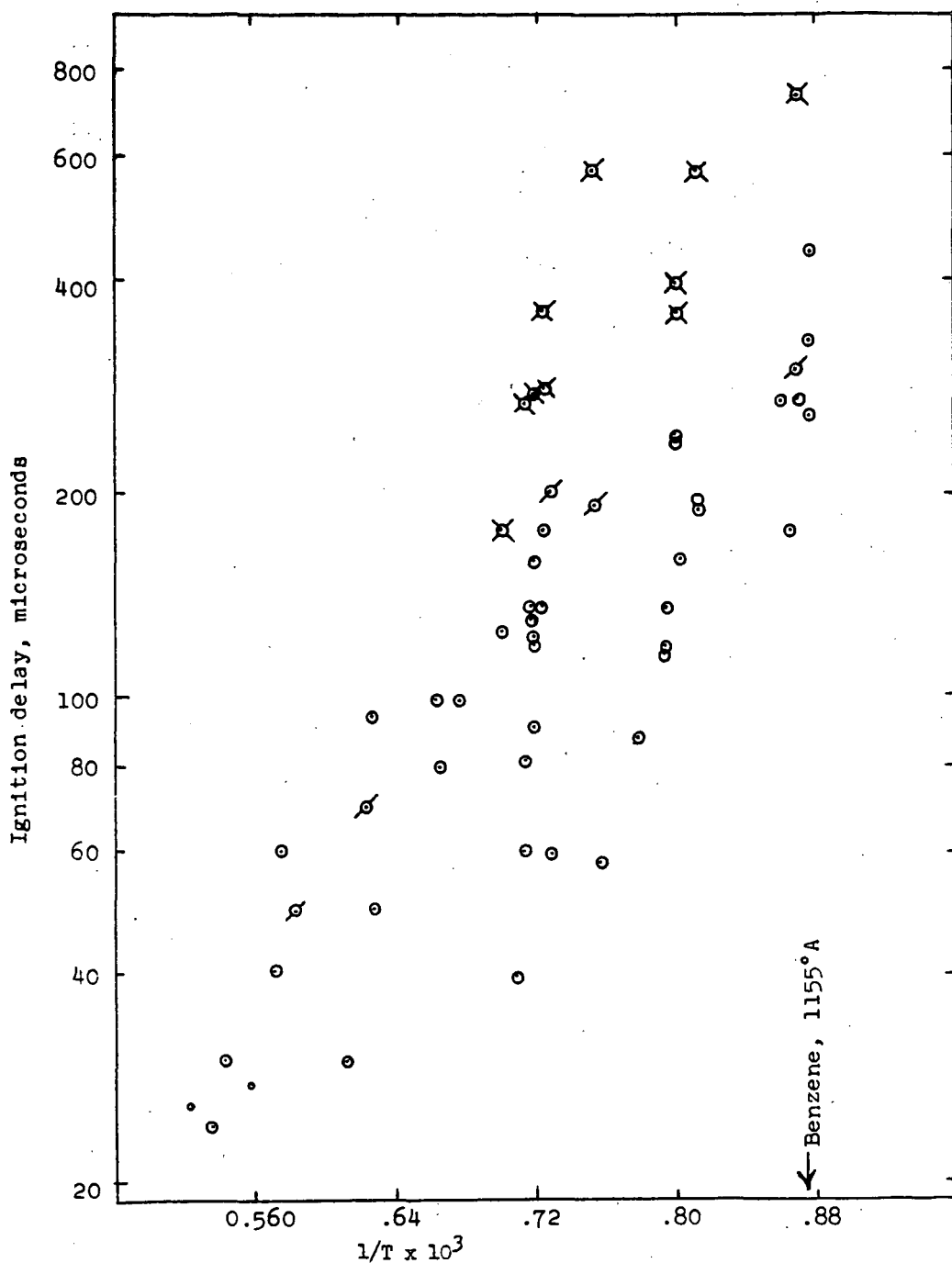


Fig. 3. Ignition of benzene-oxygen; logarithm of ignition delay versus the reciprocal of the absolute temperature. \circ Explosion; ϕ flame and explosion; \times mostly flame.